

FILED  
IN THE UNITED STATES DISTRICT COURT  
DISTRICT OF MASSACHUSETTS

2004 MAR -3 P 2: 28

SAINT-GOBAIN CERAMICS AND  
PLASTICS, INC.,

Plaintiff

v.

COORSTEK, INC.,

Defendant.

U.S. DISTRICT COURT  
DISTRICT OF MASS.

Civil Action No.:

04-40034-1

**COMPLAINT AND JURY DEMAND**

**Nature of this Action**

1. This is an action for infringement of United States Patent No. 6,669,871 (the “’871 patent”), issued on December 30, 2003 and assigned to Saint-Gobain Ceramics and Plastics, Inc. (“Saint-Gobain”). A copy of the ’871 patent is attached as Exhibit A.

**Parties**

2. Plaintiff Saint-Gobain is a Delaware corporation having a principal place of business at One New Bond Street, Worcester, Massachusetts 01615.

3. On information and belief, Defendant CoorsTek, Inc. (“CoorsTek”) is a Delaware corporation having a principal place of business at 16000 Table Mountain Parkway Golden, Colorado 80403.

RECEIPT # 404277  
AMOUNT \$ 150.00  
SUMMONS ISSUED ✓  
LOCAL RULE 4.1 ✓  
WAIVER FORM ✓  
MCF ISSUED ✓  
BY DPTY. CLK. S. Jones  
DATE 3-3-04

**Jurisdiction and Venue**

4. This action arises under the patent laws of the United States, Title 35 of the United States Code.

5. This Court has subject matter jurisdiction pursuant to 28 U.S.C. § 1338(a).

6. Venue in this district is proper pursuant to 28 U.S.C. § 1391(b) and § 1400(b).

On information and belief, CoorsTek has transacted business, committed acts of infringement, and induced and contributed to acts of infringement in the District of Massachusetts and this action arises from the transaction of that business and that infringement. On information and belief, CoorsTek also systematically and continuously conducts substantial business in the District of Massachusetts.

**Count I**  
**(Patent Infringement)**

7. Saint-Gobain repeats and realleges the foregoing paragraphs.

8. Saint-Gobain is the owner of the '871 patent and has the right to sue on the '871 patent.

9. Defendant CoorsTek has infringed, and is continuing to infringe, literally and/or by equivalents, the '871 patent by making, selling, offering to sell, and using within the United States goods covered by one or more of the claims of the '871 patent.

10. Defendant CoorsTek is inducing and contributing to infringement by others of the '871 patent, literally and/or by equivalents, by causing others to make, use, sell, or offer to sell goods covered by the '871 patent within the United States.

11. Defendant CoorsTek's infringement of the '871 patent is and has been willful, has caused and will continue to cause Saint-Gobain to suffer substantial damages, and has caused and will continue to cause Saint-Gobain to suffer irreparable harm for which there is no adequate remedy at law.

**Relief Requested**

WHEREFORE, Saint-Gobain requests that this Court:

1. enter a preliminary and permanent injunction enjoining CoorsTek and its affiliates, subsidiaries, officers, directors, employees, agents, representatives, licensees, successors, assigns, and all those acting for any of them or on their behalf, or acting in concert with them, from further infringement of the '871 patent;
2. award Saint-Gobain compensatory damages and its costs and interest;
3. award Saint-Gobain treble damages for CoorsTek's willful infringement of the '871 patent;
4. award Saint-Gobain its reasonable attorneys' fees under 35 U.S.C. § 285 or other applicable statutory or common law; and
5. award Saint-Gobain such other relief as the Court deems just and proper.

**Jury Demand**

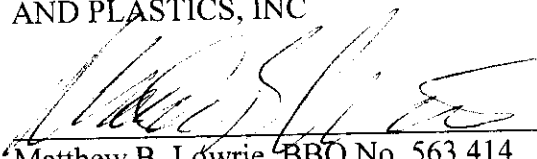
Saint-Gobain demands a trial by jury on all issues so triable.

Respectfully submitted,

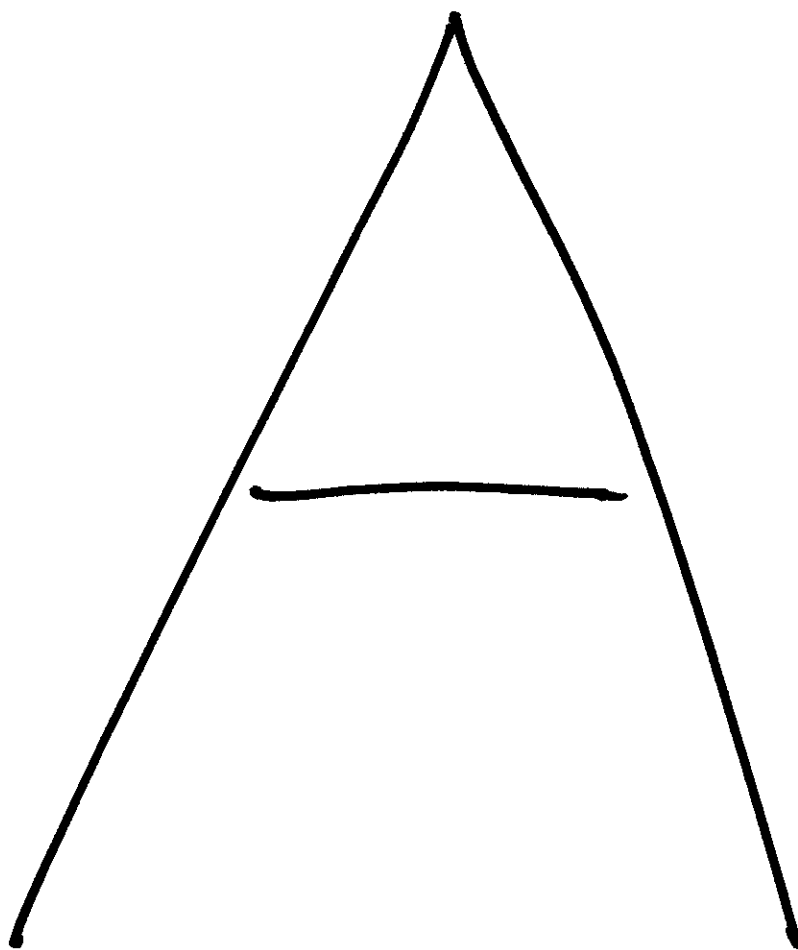
SAINT-GOBAIN CERAMICS  
AND PLASTICS, INC

March 3, 2004

by:



Matthew B. Lowrie, BBO No. 563,414  
Aaron W. Moore, BBO No. 638,076  
Lowrie, Lando & Anastasi, LLP  
Riverfront Office Park  
One Main Street - 11th Floor  
Cambridge, MA 02142  
Tel : 617-395-7000  
Fax: 617-395-7070





US006669871B2

(12) **United States Patent**  
**Kwon et al.**

(10) **Patent No.:** **US 6,669,871 B2**  
 (45) **Date of Patent:** **Dec. 30, 2003**

(54) **ESD DISSIPATIVE CERAMICS**

(75) **Inventors:** **Oh-Hun Kwon**, Westboro, MA (US);  
**Matthew A. Simpson**, Sudbury, MA  
 (US); **Roger J. Lin**, Framingham, MA  
 (US)

(73) **Assignee:** **Saint-Gobain Ceramics & Plastics,**  
**Inc.**, Worcester, MA (US)

(\*) **Notice:** Subject to any disclaimer, the term of this  
 patent is extended or adjusted under 35  
 U.S.C. 154(b) by 50 days.

(21) **Appl. No.:** **09/988,894**

(22) **Filed:** **Nov. 19, 2001**

(65) **Prior Publication Data**

US 2002/0177518 A1 Nov. 28, 2002

**Related U.S. Application Data**

(60) Provisional application No. 60/252,295, filed on Nov. 21,  
 2000, and provisional application No. 60/303,655, filed on  
 Jul. 6, 2001.

(51) **Int. Cl.<sup>7</sup>** ..... **H01B 1/08**

(52) **U.S. Cl.** ..... **252/520.21; 252/521.1;**  
 501/103

(58) **Field of Search** ..... **252/520.2, 520.21,**  
**252/520.5, 521.1, 519.5; 501/103**

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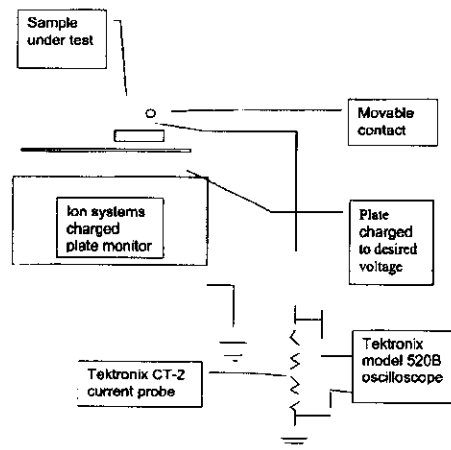
*Primary Examiner*—Mark Kopec

(74) *Attorney, Agent, or Firm*—Toler, Larson & Abel, LLP

(57) **ABSTRACT**

This invention relates to a dense ceramics having ESD  
 dissipative characteristics, tunable volume and surface resis-  
 tivities in semi-insulative range ( $10^3$ – $10^{11}$  Ohm-cm), sub-  
 stantially pore free, high flexural strength, light colors, for  
 desired ESD dissipation characteristics, structural reliability,  
 high vision recognition, low wear and particulate contami-  
 nation to be used as ESD dissipating tools, fixtures, load  
 bearing elements, work surfaces, containers in manufactur-  
 ing and assembling electrostatically sensitive  
 microelectronic, electromagnetic, electro-optic components,  
 devices and systems.

**70 Claims, 2 Drawing Sheets**



## US 6,669,871 B2

Page 2

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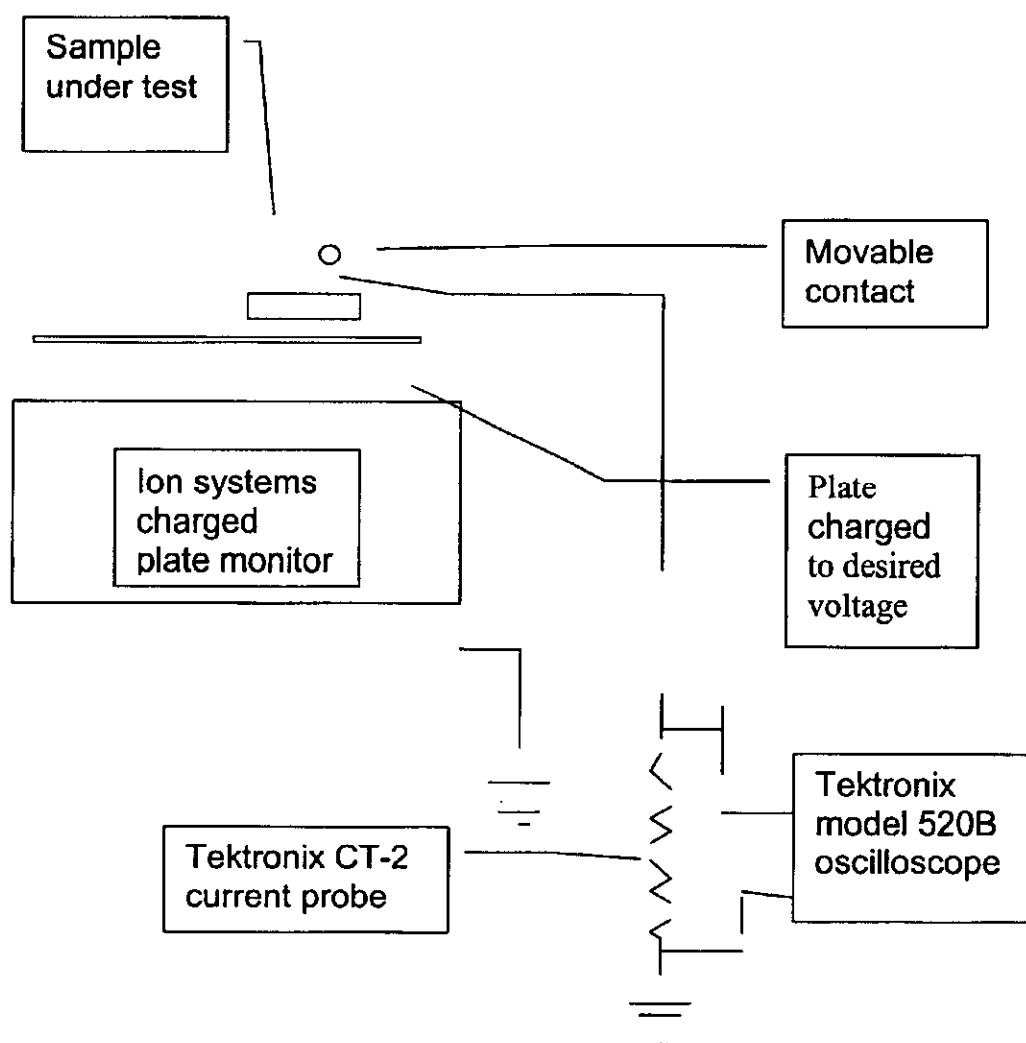
**U.S. Patent**

**Dec. 30, 2003**

**Sheet 1 of 2**

**US 6,669,871 B2**

**Figure 1**





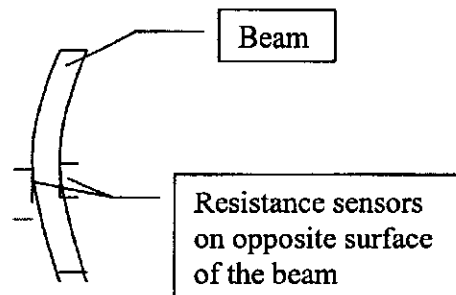
**U.S. Patent**

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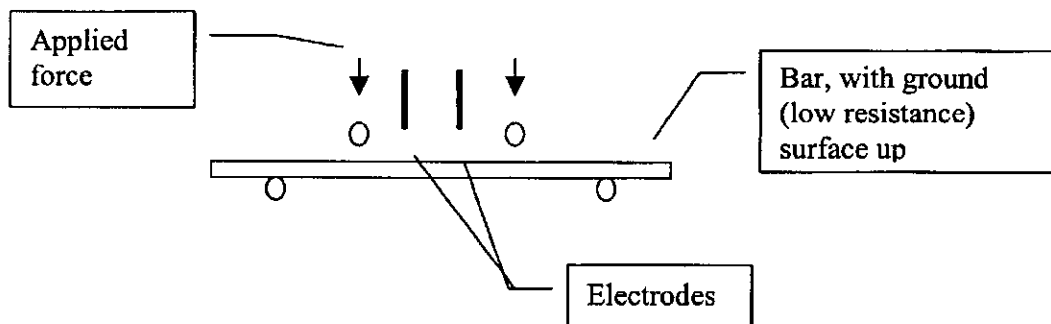
**Sheet 2 of 2**

**US 6,669,871 B2**

**Figure 2**



**Figure 3**



US 6,669,871 B2

1

## ESD DISSIPATIVE CERAMICS

## PRIORITY CLAIM

This application claims domestic priority from two commonly owned copending U.S. Provisional Patent Applications, namely U.S. Ser. No. 60/252,295, filed Nov. 21, 2000 and U.S. Ser. No. 60/303,655, filed Jul. 6, 2001. The disclosures of these two applications are hereby incorporated herein by reference.

## BACKGROUND OF THE INVENTION

An extensive background on electrostatic discharge (ESD) may be found on the Internet at the website of the ESD Association, 7900 Turin Road, Building 3, Suite 2, Rome, N.Y. 13440-2069. See "www.esda.org" for this information.

A number of ESD dissipating tools and containers have been devised and used to prevent ESD events and protect sensitive microelectronic devices. It is known that the ESD dissipating materials should not be fully insulative or conductive. Rather such materials should be semi-insulative (having a Volume Resistivity or "Rv" ranging from  $10^3$ – $10^{11}$  Ohm-cm). For example, ESD dissipating materials have been suggested in manufacturing and testing MR/GMR heads and assembling hard disk drives.<sup>1,2</sup> Similarly, ESD dissipating ceramic and carbon loaded polymer tweezers have been used in handling semiconductor parts.

The use of semi-insulative ceramics has been reported for some ESD control applications. In general, semi-insulative ceramics were prepared by mixing conductive or semiconductive ceramics with insulative ceramics, which is a similar manufacturing method to those of ESD dissipative polymers. In the past, some semi-insulative materials were prepared for other applications based on the mixing rule. For example, U.S. Pat. No. 3,410,728 reports that metal oxide doped stabilized zirconia have both ionic and electric conductivities at elevated temperature.  $\text{LaCrO}_3$  doped stabilized zirconia<sup>3</sup> has also been tried for a high temperature electrical conductor.

Recently, German Patent No. 3743630 C1 (1989)<sup>4</sup> reported that tweezers made out of various ceramics having surface resistances of  $10^5$ – $10^{10}$  Ohms can be used to hold electrostatically sensitive components to protect against electrostatic discharge. The patent further indicated that partially or fully stabilized, zirconia based ceramics can be used as a base material. However, the patent did not disclose any information about manufacturing process and other physical properties.

Japanese Patent Application No. JP62-25404 A (1987)<sup>5</sup> reported that the resistivity of stabilized zirconia can be controlled in the range of  $7 \times 10^2$ – $5.5 \times 10^5$  Ohm (the resistance value can not be converted to resistivity without electrode dimensions) at 600° C. by adding 5–50 mol. % of transition metal oxide ( $\text{Co}_2\text{O}_3$ ) for thermistor elements. Again, the patent did not disclose any information about other physical properties.

Japanese Patent Application No. JP3-5363 A (1991) reported that ceramic tape guides made from a mixture of  $\text{TiO}_2$  (50–99 wt. %) and  $\text{Al}_2\text{O}_3$  can be heat treated in various atmosphere to volume resistivities of  $10^4$ – $10^{11}$  Ohm-cm to protect the magnetic tape drive from electrostatic discharge damage. The tape guide is more resistant against wear due to its higher hardness of 700–900 Kg/mm<sup>2</sup> compared to conventional tape guides made out of stainless steel.

U.S. Pat. No. 5,612,144 (1997)<sup>6</sup> reports that alumina and silicon carbide based ceramics having resistivities of  $2 \times 10^9$

2

to  $10^{10}$  Ohm/cm<sup>2</sup> can be prepared by adding nitrides and carbides of Ti, Zr, Hf, Nb and Ta for electrification removing components.

U.S. Pat. No. 5,830,819 (1998)<sup>7</sup> reported alumina composite ceramics with volume resistivities from  $1 \times 10^7$  to  $1 \times 10^{13}$  Ohm-cm at 25–75° C. and an absolute value of the temperature coefficient of volume resistivity (TCR) of not larger than 1.8%/° C. can be prepared with additives containing transition metal oxides such as  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{MnO}_2$ ,  $\text{NiO}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{V}_2\text{O}_5$  for antistatic part such as conveyer arm, handling jig, tweezers for holding wafers.

U.S. Pat. No. 5,958,813 (1999)<sup>8</sup> reports that semi-insulating aluminum nitride (AlN) sintered body can be made to the resistivity of  $10^4$  to  $10^{11}$  by forming an intergranular phase from at least one oxides of Ti, Ce, Ni, Ta, Y, Er and Yb, or from Si to prepare a member for removing static electricity.

Most materials described above are not necessarily structurally reliable for high performance ESD dissipative ceramic tools because of low flexural strength, fracture toughness and residual porosities in their microstructure. PCT Patent Publication No. WO 98/49121 (1998) reports that semiconductive zirconia with good mechanical properties can be prepared using 10 to 40 wt. % oxides of Fe, Co, Ni, and Cr.

Japanese Patent Application No. JP8-39441 (1996) reported that tweezers with volume resistivities of  $5 \times 10^7$  to  $1 \times 10^9$  Ohm-cm can be used to hold semiconductor parts to avoid ESD problems.

C. Lam (1996)<sup>9</sup> has reported that the ESD dissipative polymers and ceramic tweezers can be used during the manufacturing and handling of MR heads. The test result indicated that tweezers made out of a "doped" zirconia (vendor proprietary) showed the best performance.

Japanese Patent Application No. JP 10-296646 A (1998) reported a high strength, zirconia based composite tweezers with flexural strength of greater than 700 MPa and resistivities of  $10^6$ – $10^9$  Ohm-cm. Further, the material showed a residual magnetic flux of up to 14 Gauss.

U.S. Pat. No. 6,136,232 (2000) reports that some perovskite type oxides can be mixed with stabilized zirconia to prepare electrostatic dissipative ceramics. The patent also describes that other perovskite type oxides react with zirconia to form zirconates, thus not satisfactory for electrostatic dissipative ceramics. The patent though reports only volume resistivities as a key property.

U.S. Pat. No. 6,274,524 (2001) claims a semiconductive zirconia body formed under oxidative conditions, comprising 60 to 90 weight % of  $\text{ZrO}_2$  including stabilizing agent, said zirconia body having no more than 2% by weight  $\text{Al}_2\text{O}_3$ , containing greater than 10 weight % to 40 weight % of one kind or more of oxides of Fe, Co, Ni, and Cr as conductivity giving agents, having a three-point flexural strength of at least 580 MPa, and having a volume specific resistance of  $10^6$  to  $10^9$  Ohm-cm.

The above prior art attempts at control of ESD have not been fully successful in satisfying either current ESD dissipative requirements or the predicted future requirements for ESD dissipative ceramics, for the following reasons:

1. The Prior Art Lacks Sufficient High Density

ESD dissipative ceramic compositions of the prior art to date have not had sufficiently high density (i.e., 97–99% T.D.). This is due to processing techniques used in the prior art, which have not included hot isostatic pressing (hereinafter "HIPing"). The prior art has typically not made hot isostatically pressed (hereinafter "HIPed") materials due

US 6,669,871 B2

3

to thermochemical instabilities which during a typical HIPing process. The conductivity modifiers employed in the prior art ESD dissipative ceramics often undergo a thermochemical reduction during a HIPing at high temperature (1200°–1500° C.) and high argon pressure (100–250 MPa) in a HIP using graphite heating elements. The thermochemical reaction during the HIPing reduces transitional metallic oxides to oxygen deficient metallic oxides by releasing gases (CO<sub>2</sub> or O<sub>2</sub>) from the body to the surface resulting in bloating and cracking of ceramic bodies.

Pressureless sintered ESD dissipative ceramics have a number of pores (pits) on the surfaces and inside of bodies. For instance, sintered ceramics with 99% TD may have a number of pores of 0.1–10  $\mu$ m diameters. Assuming a square sintered plate with dimensions of 1 cm×1 cm×0.25 cm, 99% T.D., and monosized pores of 1  $\mu$ m diameter the number of exposed pores on the surface are 10 millions. Often these pores trap particulate debris and contaminants inside, thus difficult to clean and act as the source of contamination during the use of such components in clean room environments. Further, the cleaning of ceramics with residual pores is difficult compared to that of substantially pore free ceramics by HIPing. On the other hand, the number of pores on HIPed ceramic plate with the same dimension and 99.9% T.D. would be 1 million reducing the number of defect (residual pores) to 1/10 of the sintered plates.

In addition, the residual pores may interact with diamond grits of grinding wheels during the machining into final shapes and dimensions resulting in damaged spots, which is a potential source of particulate debris over the life time of such components.

It is, therefore, highly desirable to prepare a ceramic composition which is easy to densify by a conventional hot isostatic press (HIP) to achieve fully dense, structurally reliable ceramic components.

## 2. The Prior Art Lacks Sufficient High Strength

The HIPing also further eliminates strength limiting cavities and pores in ceramic bodies resulting in structurally stronger and more reliable components. It is well known that the flexural strength of ceramic components can be improved after HIPing by greater than 20% up to over 50%. Accordingly, HIPing is a preferred processing step to prepare high strength, mechanically reliable components and enable a thinner cross section and complicated shapes.

In summary, HIPable ESD dissipative ceramics are advantageous for an improved contamination control in the fab due to the absence of residual pores.

## 3. The Prior Art Lacks Choices of Color

Modern manufacturing techniques involve a number of automated processing steps. The efficiency of vision system in such an automated manufacturing system is critical. The high productivity of vision system can be achieved by a fast optical recognition from differences in colors and contrast. The color of magnetic recording heads is substantially black due to the color of slider material (AlTiC, a composite of titanium carbide and alumina). Therefore, a "non-black" ESD dissipative material is highly preferred in order to ensure higher productivity in vision systems. The color of other microelectronic components may vary. Therefore it is desirable to have various color capabilities with ESD dissipative ceramic tools and fixtures. Most prior art ESD dissipative ceramics commercialized to date have been either black or substantially dark.

## 4. The Prior Art Lacks Tunability

The proper ESD dissipation for a specific application can be obtained by a material with a specific volume/surface resistivity. However, there exist a number of different appli-

4

cations requiring a broad range of surface resistivities as reported. In the prior art, the control of volume and surface resistivities has been obtained mainly by a compositional variation in ESD dissipation. Therefore, one should prepare various compositions of materials to satisfy various application needs, each of which may require different resistivities. In addition, the amount of resistivity modifier used in forming composites often tends to make appreciable changes in other material properties. The design engineer thus tends to modify the resistivity specification for the application based on test results. Accordingly, there is a need for a material having a tunable resistivity.

## 5. The Prior Art Lacks Sufficient Nonmagnetic Properties

For some applications, especially in GMR head manufacturing, it is desirable to have the lowest magnetic susceptibility of the ESD dissipative material. For other applications to measure electromagnetic performance of microelectronic devices requires no interference from fixtures. Most transition metal based resistivity modifiers exhibit a substantial magnetic susceptibility. It is reported in PCT Publication No. WO 98/49121 that a residual magnetic flux density of up to 16 Gauss is satisfactory for general ESD dissipative applications. However, there is a need for a substantially nonmagnetic material to be used in tools for electromagnetic measurements. Accordingly, for some applications, it is preferable to have an ESD dissipative material made with one or more substantially nonmagnetic resistivity modifiers.

The surface resistivity is not the only measure to determine the performance of ESD dissipative materials. In general, it is very desirable to have a fast dissipation of static charges from the contact at the surface. A more precise measure is a charge decay time in ms as described in the literature.

PCT Publication No. WO 98/49121 reports that an acceptable decay time from 1000 to 100 V is 0.1–20 seconds. Further, they reported that materials outside of that range are not suitable for ESD dissipative ceramics. However, it has been noted that a decay time of less than 0.1 second is preferred for most ESD dissipative applications.<sup>10</sup>

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates the apparatus employed in the examples to take measurements of transient current of sample materials.

FIG. 2 illustrates the apparatus employed in the examples to measure the resistance of sample materials in two locations—one stressed and one not stressed.

FIG. 3 illustrates the apparatus employed in the examples to measure the effect of perturbations on conductivity of sample materials.

## SUMMARY OF THE INVENTION

One object of the present invention to provide ESD dissipative ceramics which are multifunctional, and capable of dissipating static electricity in contact during manufacturing of sensitive microelectronic devices, and uses. It is known that such ESD dissipative materials must have intermediate resistivities. For instance, the surface resistivity should range from 10<sup>3</sup> to 10<sup>11</sup> Ohm-cm, preferably from 10<sup>4</sup> to 10<sup>10</sup> Ohm-cm, more preferably from 10<sup>5</sup> to 10<sup>9</sup> Ohm-cm and most preferably from 10<sup>6</sup> to 10<sup>8</sup> Ohm-cm. These values are desirable in order to dissipate electrostatic charges. The second requirement is the dissipation characteristics. For instance, the charges must be dissipated fast enough through the volume of part. In addition, the material must be suffi-

US 6,669,871 B2

5

ciently homogeneous to dissipate the charges evenly to avoid hot spots.

Another object of present invention is to provide a tunable resistivity in a material to meet various resistivity needs for a number of applications.

A further object of this invention is to provide various colored ESD dissipative ceramics, especially with substantially light colored ceramics.

A still another object of this invention is to provide HIP-able ESD dissipative ceramics with substantially lower residual porosity compared to the pressureless sintered ceramics for high mechanical reliability, low contamination, and good machinability.

A special object of the current invention is to provide substantially non-magnetic ESD dissipative ceramics for safer uses for various applications of electromagnetic measurements.

Accordingly, the present invention is directed to high-density ceramics (i.e., greater than 99% of theoretical density or "TD") suitable for ESD-dissipation applications. In more preferred embodiments, the density of the ceramics is greater than 99.5% of the theoretical density. Such ceramics have a volume resistivity in the range of  $10^5$ – $10^{10}$  ohm-cm, and also have high strength (i.e., greater than 500 MPa). These ceramics are formed by sintering in air and then, if necessary or desired, by hot isostatic pressing ("HIP" or "HIPing") wherein the HIP environment is preferably not oxidizing. A second heat treatment (either sintering and/or HIPing) is designed to produce one of the following results:

(1) it may raise the resistance; or

(2) it may lower the resistance;

such that the volume resistivity shifts (or moves higher or lower) into the range  $10^5$ – $10^9$  ohm-cm.

In certain preferred embodiments, the ceramics are prepared from stabilized  $ZrO_2$ , advantageously with one or more conductive or semi-conductive additives selected from the group consisting of metal oxides, metal carbides, metal nitrides, or combinations thereof. Advantageously, component parts made using these ceramics have a decay time of less than 2 sec.

In certain preferred embodiments, the ceramics have a hardness greater than 8.5 GPa Vickers; with K<sub>1c</sub> greater than 4 MPa m<sup>-1/2</sup> and contain ZnO, preferably in range 15–25% (vol % of initial reagents) thereby forming a "light" color ceramic. Some preferred embodiments contain ZnO and up to about 10% (vol.) of a transition metal oxide. For example, manganese oxide (1–8 vol %) works well to produce a "dark" colored ceramic.

Some preferred embodiments contain SnO<sub>2</sub>, preferably in range 20–80% (vol % of initial reagents). Other preferred embodiments contain ZrC or barium hexaferrite in the range 15–35 vol %.

In certain preferred embodiments, the ceramics have an MOR retention of more than 50% after heat treatment in water at 200–250° C. under equilibrium partial pressure.

According to another preferred embodiment, there is provided a particulate composite based on Y-TZP product 15–40% ZnO or 15–60% doped-SnO<sub>2</sub> for light colored ESD dissipating ceramics. The terms "light colored" means that the ceramic material is not black or another dark color. Preferred light colored materials are white, off-white, light grey, tan, and the like.

Unlike most electrically conductive metals, ceramics exhibit a wide range of electrical conductivities and resistivities. Ceramics are insulative, semiconductive and conductive in its bulk properties. The electrical resistivity can be

6

tailored by doping conductive or semiconductive phases in insulative phases. Accordingly, resistivity modifiers have been widely used to tailor conduction properties of materials. There exist a number of well-known conductive ceramic families for such tailorability. The modifier could be reactive or non-reactive with base materials.

Although there is no single ceramic material that completely satisfies the long wish list of properties for ESD dissipation, it is known that zirconia ceramics can satisfy a good number of requirements excluding electrical properties. A number of insulative Y-TZP (yttria partially stabilized tetragonal zirconia polycrystals) parts have been accepted and used for various tools to manufacture magnetic recording heads to date due to its reliable mechanical properties. Other TZPs by other known stabilizers such as rare earth oxides, MgO, CaO, and mixtures thereof can be used as a matrix material.

Zirconia is insulative ( $R_v=10^{13}$  Ohm-cm) at room temperature. It has been well known that a conductive zirconia composite can be made by dispersing conductive particles to form electrodischarge machinable (or EDMable) compositions. Typically, particulate dispersoids of metallic conductivity are known to be very effective, such as carbides, borides, and suicides resulting in typical resistivities of less than 1 Ohm-cm, which is too low resistivities for optimum ESD dissipation.

Conductive oxides have also been tried to optimize the electrical resistivity of zirconia, such as transition metal oxides, Fe<sub>2</sub>O<sub>3</sub>, Co<sub>2</sub>O<sub>3</sub>, NiO, Cr<sub>2</sub>O<sub>3</sub>, etc. It has been reported<sup>11</sup> that 3–15 mol. % iron oxide can be doped to yttria-stabilized ceramics to provide an electrical resistivity of  $\sim 10^5$  Ohm-cm at 250° C. See also Kyocera's Japanese Patent Applications, cited above. However, some oxide additives alter the transformability of Y-TZP, deteriorating the fracture toughness. Transition metal oxides act as colorant in zirconia, forming characteristic dark colors. Thus, these additives are not satisfactory for a white/light colored material.

In addition, these transition metal oxides are subjective to thermochemical redox reactions during the high temperature process such as sintering and HIPing. For instance, Fe<sub>2</sub>O<sub>3</sub> in zirconia undergoes a thermochemical reduction during HIPing in inert gas, such as Ar, resulting in the formation of pores or cracking from gas forming reaction. HIPing in oxygen bearing gases prohibits such deleterious reactions but it is not cost effective due to high cost of platinum heating element and special kiln furniture.

Both conductive and semiconductive phases can be used as resistivity modifier to tailor the resistivity and dissipation characteristics. Some resistivity modifier can react with Y-TZP to form new phases resulting in insulative properties and/or changing the transformability of Y-TZP. Such modifiers must be avoided. In addition, the resistivity modifier should satisfy an many requirements as possible listed below to be successfully used in various applications:

Pressureless sinterability and sinter-HIPability, good machinability, and structural reliability

Various colors, preferably a light color

Lowest particle generation

Tunable ESD properties

Lowest corrosion in processing environments,

Substantially non-magnetic or strongly magnetic.

It has been found that light colored ESD dissipative ceramics can be prepared by dispersing ZnO grains in Y-TZP matrix. Further, doped SnO<sub>2</sub> in Y-TZP is also effective to achieve a light colored material with the desired resistivity.



US 6,669,871 B2

7

A few dark colored (or black) ESD dissipative ceramics have also prepared by adding  $\text{LaMnO}_3$ ,  $\text{LaCrO}_3$ ,  $\text{ZrC}$  and  $\text{BaFe}_{12}\text{O}_{19}$  in Y-TZP.

Magnetic susceptibilities of resistivity modifiers may vary. (The magnetic susceptibility is defined as the ratio of the intensity of magnetism induced in a material to the magnetizing force or intensity to field to which is subjected.)  $\text{ZnO}$ ,  $\text{SnO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrC}$  and  $\text{SiC}$  have very low molar magnetic susceptibility of less than  $10^{-4}$  ml/mol. On the other hand,  $\text{Fe}_2\text{O}_3$  and  $\text{BaFe}_{12}\text{O}_{19}$  exhibit high molar magnetic susceptibility of greater than  $10^{-2}$  ml/mol. Some materials such as  $\text{LaMnO}_3$  and  $\text{LaCrO}_3$  show medium molar magnetic susceptibility. The modifiers with low magnetic susceptibility is good for applications requiring low electromagnetic interference. On the other hand, modifiers with high magnetic susceptibilities can be used in applications requiring magnetic functions.

It has been found that the resistivity of some materials significantly change after HIPing. Further, the resistivities of HIPed ceramics can be controlled to a desired values by a controlled heat treatment in air or controlled atmosphere.

Finally, the volume percentages (Vol %) of ingredients disclosed herein are based upon currently available commercial grades of materials. These numbers may be varied if other materials are employed—e.g., nano-size particles would result in lower Vol % values.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As described above, the present invention seeks to solve the problems noted above in the prior art ESD dissipative materials. Accordingly, the present invention provides a strong ESD dissipative material, having high density, preferably formed by HIPing, and a choice of colors, particularly lighter colors than black. The ESD dissipative material of the present invention further has "tunable" resistivities, namely selectable during preparation, with mechanical reliability of components, low contaminating surface, and low magnetic susceptibility.

Preferably, the ceramic compositions of the present invention have ESD dissipative characteristics, tunable volume and surface resistivities in the semi-insulative range.

Preferably, the ceramic compositions of the present invention may also include a small amount (e.g., less than about 2 wt. %) of one or more sintering aids or additives selected from the group consisting of  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{SrO}$ ,  $\text{BaO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{CuO}$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{CeO}_2$ ,  $\text{Y}_2\text{O}_3$  and mixtures thereof. The amount of additives must be small enough not to alter desirable properties for ESD dissipative ceramics. In some cases, limited amounts of these oxides may be incorporated from raw materials and/or contamination during the powder processing.

Preferably, the ceramic compositions of the present invention are substantially pore free, particularly in relative numbers, e.g., more than 90% pore free—based upon pore sizes greater than  $0.5 \mu\text{m}$ . As used herein, the terms "pore free" and "substantially pore free" may also be defined as a relative density greater than 99%, most preferably greater than 99.5%.

Preferably, the ceramic compositions of the present invention have high flexural strength. Sinter-HIPed TZP materials with  $\text{ZnO}$ ,  $\text{SnO}_2$ ,  $\text{LaMnO}_3$ , and  $\text{LaCrO}_3$  are stronger 1,000, 650, 716, and 1,005 MPa, respectively.

Preferably, the ceramic compositions of the present invention have a color lighter than black. As used herein, the preferred "light" color is defined as being lighter than the

8

midpoint of 16 grey scale as defined by ISO. Color can also be measured using a color meter for more quantitative measurements. The ceramic compositions containing  $\text{ZnO}$  and  $\text{SnO}_2$  compositions show light colors, while most others are black or very dark.

Preferably, the ceramic compositions of the present invention have a voltage decay time (a measure of the performance of ESD dissipative ceramics) of less than 500 ms, most preferably less than 100 ms.

Preferably, the ceramic compositions of the present invention have a low transient current, such as less than 100 mA, most preferably less than 50 mA.

As described above, one aspect of the present invention is the formation of ESD dissipating tools using the ceramic compositions of the present invention.

The dense product of the present invention comprises TZP as a base component and particulate dispersoids which include at least one selected from conductive or semiconductive oxides, carbides, nitrides, oxycarbides, oxynitride, oxycarbonitrides, and the like. Some resistivity modifiers were doped with additives or pre-alloyed to desired crystalline form and/or resistivities. When the amount of resistivity modifier is greater than greater than 60 vol. %, it is difficult to take advantage of high fracture toughness and flexural strength of TZP. When the amount of conductivity modifier is less than 10 vol. %, it is difficult to achieve the desired dissipating properties. Suitable ranges of resistivity modifiers thus include 15–50, 20–40 and 25–30 vol. % and include ranges that overlap these values.

The average particle sizes of all ceramic powders were smaller than  $1 \mu\text{m}$  to achieve a homogeneous microstructure and uniform electrical properties and desired dissipation characteristics. Some pre-alloyed powders were milled in a plastic jar with Y-TZP milling media to obtain desired particle size. Powders were mixed by a wet milling in a plastic jar mill with Y-TZP milling media, followed by drying and granulation.

The dense product of the invention is prepared by molding a mixture of Y-TZP powder and conductivity modifier powders into any desired shapes by any molding methods such as dry pressing, slip casting, tape casting, injection molding, extrusion, and gel casting. An organic binder system may be added into the powder mixture to achieve a high green strength for handling, green machining, and to maintain shapes during the densification.

The molded ceramics articles are debinderized and sintered in air or desired reactive or inert atmosphere to greater than 95% T.D., preferably to greater than 97% T.D. The sintered ceramics articles can be further densified by hot isostatic pressing in inert gas or oxygen bearing inert gas to full density. The thus obtained sintered or sinter-HIPed ceramic articles exhibits a volume resistivity of from  $1 \times 10^3$  to  $1 \times 10^{12}$  Ohm-cm in ambient temperature resistivities between that of an insulator and that of a semi-conductor.

Some resistivity modifiers may react with Y-TZP during sintering and/or HIPing often forming zirconate compounds with very different electrical properties. Such reaction could be much faster at high temperature as these reactions are thermally activated. Thus, it is sometimes very desirable to limit such a deleterious reaction by reducing the densification temperature and times. Another complicating reaction during sintering is that the conductivity modifier could influence the transformability of zirconia grains either stabilizing the Y-TZP grains further or destabilize the Y-TZP grains. In this case, the yttria content in zirconia may be controlled to optimize the transformability or other TZP